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The Determination of Sulphuric Acid in the Presence of Iron

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The determination of sulphuric acid in the presence of any considerable quantity of iron by the simple precipitation with barium chloride has for a long time been known to be faulty. Instead of getting a pure precipitate, a precipitate was always obtained contaminated with iron, and instead of getting a higher result than that obtained by the precipitation of pure barium sulphate, a lower result was always obtained. Numerous investigators tried to avoid this difficulty, by seeking to discover methods by which the precipitation of pure barium sulphate could be made possible; but always failed in their attempts, although they have shown clearly in what form the occluded iron in the barium sulphate exists. That it existed in the form of ferric sulphate was indicated by the loss of sulphur trioxide upon the ignition of the precipitate. So also was explained why the weight of the occluded iron was always found to stand too low.

These undeniable facts we owe to the work of Jannasch; and in the consideration of them, the method given by

C. Friedham in his Quantitative Analysis for the purification of barium sulphate which is contaminated with iron, seems absurd. According to his method the undried precipitate is at once digested with ammonium sulphide, by which the iron is transformed to ferric sulphide, which after the washing out of ammonium sulphide is "supposed" to be removed by hot dilute hydrochloric acid. As a matter of fact by this method the washing out of the ferric iron is not successful; but if it were, it is obvious that nothing would be gained in the determination of sulphuric acid. On the contrary, the error would be increased; because of the fact that the iron is contained in the precipitate as sulphate and so a doubtful amount of sulphuric acid would go into solution by the changing of the sulphate into sulphide and therefore for the purpose of analysis would be lost. But if the hydrochloric acid dissolved out the iron, the total error would still be far greater than without that"purification" of the precipitate.

Although Jannasch was the first to recognize the particular nature of the impurity of barium sulphate as iron, his discovery did not lead to a method by which to avoid

these errors. There is no doubt that the iron goes into the barium sulphate as ferric sulphate. Ferric sulphate, however, can only be precipitated in a solution which contains ferric ions and sulphuric acid ions, but the precipitation is impossible on the removal of one or both of these ions from the solution, or on their reduction to a very small concentration. Naturally we cannot remove the sulphuric acid ions as the problem is to determine the sulphur, but the disturbing ferric ions can be easily removed. This may be accomplished in two ways; either by precipitating the ions in any suitable form out of the solution, or by transforming it into a harmless complex ion.

This first method was employed by G. Lunge. He proposed first to precipitate the iron with ammonia as ferric hydroxide and then to precipitate the sulphuric acid in the filtrate. The filtering of the ferric hydroxide is tedious and gives proof that the precipitate, notwithstanding the careful washing, retains sulphuric acid very tenaciously in the form of basic sulphate, so that the precipitation after the dissolving in hydrochloric acid is again repeated several times.

This repeated operation is naturally without considering lost time, an unavoidable source of error and has been justly condemned by Jannasch. In spite of the repeated precipitations the loss of sulphuric acid is still quite large being as much as five per cent.

In Zeitschrift für Anorganische Chemie, XlX, pp. 97-103, F. W. Küster and A. Theil publish some interesting investigations which they have made on this subject. According to their work, the simple precipitation with barium chloride of sulphuric acid in the presence of iron gives results which average seven per cent below the results obtained by the precipitation of pure sulphuric acid according to the directions given by Fresenius in his Quantitative Analysis. Other experiments were made with greater and smaller quantities of ferric chloride, whereby they found that the amount of ferric chloride and the loss in weight of barium chloride were parallel. Kuster and Theil have applied the method used by G. Lunge, trying to avoid entirely the laborious and difficult filtering and washing of ferric hydroxide. They precipitated the iron

with ammonia as ferric hydroxide; then without regard to the precipitate already formed, they precipitated the solution further with the necessary quantity of barium chloride, and then dissolved the ferric hydroxide with hydrochloric acid. The small amount of sulphuric acid enveloped in the ferric hydroxide is transformed into barium sulphate without any noticeable loss in weight. Very good results are obtained by working according to this method, giving an average not more than five one-hundredths of a per centbelow that obtained by the determination of pure sulphuric acid.

Küster and Theil also worked out methods proving the practicability of the way indicated by theory. As was explained before, this method consists in removing the ferric ions present in the solution by making the ion the constituent of the complex ions. The latter happens by the addition of oxalates, from the fact that iron cannot be precipitated from a solution of oxalates with ammonia. According to this method the solution of sulphuric acid and ferric chloride is treated with ammonium oxalate and further precipitated with requisite amount of hot barium

chloride and treated with hydrochloric acid. The precipitate obtained by this method was nearly pure white, and in four experiments agreeing very closely among themselves, results were obtained which were only eleven one-hundredths of a per cent too small as compared with the precipitation of pure sulphuric acid.

The iron present in the solution is therefore when present in a complex ion not occluded in the barium sulphate. Küster and Theil have obtained this result which has been sought in vain by so many investigators, solely by using Jannasch's results together with the application of the ion theory to the problem in question. This theory was pointed out years ago by a specialist named Ostwald, and has allowed itself to be applied to solving most successfully the unknown problems in analytical chemistry, and especially has it cleared up points and suggested new lines of work. This theory, however, is not comprehended by some chemists, who make themselves acquainted only superficially with it. Iron also enters into the molecule of tartaric acid in the form of complex ions. A series of experiments were therefore performed by Küster and Theil

only that oxalates were replaced by tartrates. Kuster and Theil performed four experiments which gave an average agreeing exactly with the normal results. The actual application of the ammonium tartrate method is not recommended as practical, as it is not so convenient and reliable as the other method and the results vary as much as two-tenths per cent from the correct value. It was worked out by Kuster and Theil to show the harmlessness of the iron in complex ions, and so verify the correctness of their assumption in applying the ion theory to this problem; and it is certainly obvious that the determination of sulphuric acid in the presence of iron can be made by transforming it into a complex ion.

In Zeitschrift fur Anorganische Chemie, XIX, p. 454 an answer was published by G. Lunge, to whom reference has been previously made, in defence of his method against the more recently suggested methods of Kuster and Theil. Lunge first criticises Kuster and Theil for obtaining an error of seven per cent in their determination of sulphuric acid in the presence of iron by the simple precipitation with barium chloride. He remarks that he has never found

mistakes in his experiments exceeding one to two per cent. These criticisms, however, seem unnecessary, for it is very improbable that analysts like Küster and Theil would make such mistakes as seven per cent when only five-tenths per cent are allowed. It shows clearly that Lunge has a different motive in view than have Küster and Theil. Lunge is concerned in the practical side of the question, while Küster and Theil are concerned only in solving the scientific problem. According to Jannasch it is evident that the iron is precipitated in the barium sulphate as ferric sulphate. How this precipitation takes place is not understood, and was the point Küster and Theil tried to clear up. When one wishes to find out his mistakes, he must try to make them as great as possible, because in case of a little mistake the magnitude of it is lost in the experimental error. By working with a rather concentrated solution, and precipitating hot and slowly, Küster and Theil thought that the formation of a relatively coarse-grained precipitate would take place and that the subsequent dissolving out of ferric salts which, according to the law

of distribution occur more abundantly on the inside of the grain, was impossible.

Lunge next brings up the question of time in his reply. He maintains that Küster and Theil's method of precipitating with ammonia is tedious and in no way less troublesome than his, and takes four hours, while his takes but from three-fourths to one hour. Although Küster and Theil did not propose any method for practical purposes, yet it is clear that Lunge's assertion is untrue. First in regard to the time, especially in technical work which Lunge emphasises principally, it takes from the beginning of the analysis until its completion. The amount of time one has to spend on the analysis is much more important. When one allows the precipitate to stand four hours so that it may become coarse-grained one cannot reckon this time as being employed on the analysis, because the skillful analyst makes steadily so many analyses that the time between operations would be entirely employed. After a little experience he would be able to shorten the time given for each lengthy digestion, for the precipitate can be handled within much less time, the lengthy digestions

being given only to insure safety.

The operations in Lunge's method and in that of Küster and Theil are identical until the removal of the iron hydroxide. Lunge filters and washes carefully the iron precipitate which according to his directions takes about one hour, while Küster and Theil dissolve it with a few drops of hydrochloric acid, which requires only a few minutes, and is less awkward. It is plain to see that the four and one half hours employed by Küster and Theil are unnecessary. They only allowed the precipitate to stand so that it would become granular and would filter better. They had no intention whatever of selecting a shorter time, as they had not the slightest idea of proposing a method; their aim being merely to show that their theory led to correct results.

The last remark of Lunge's is that Kuster and Theil's methods are unnecessary. This remark is uncalled for, since Küster and Theil's investigations have not been in vain as they have at least cleared up an interesting even if only theoretical question in Analytical Chemistry.

It is only a matter of taste which method is chosen for technical work. Some chemists consider it neater to remove the iron by mechanical filtration than to make the iron harmless by means of an analytical artifice, but it is certainly evident that the filtering out of the ferric hydroxide is useless. Lunge's communication criticising Küster and Theil's work shows that their distinct purpose is misunderstood throughout, and he has unduly emphasised trivial points. To Küster and Theil it is quite unimportant which method is used for the analysis of pyrite in technical work, and everyone who reads their articles impartially will get the impression that it was their purpose not to show a new and practicable method, but to show how important it was for the analyst to know the newer views of the nature of the salt solution in the treatment of his problems, and to solve the problems of determining sulphuric acid in the presence of iron by precipitating with barium chloride.

An interesting communication has been published in Zeitschrift für Anorganische Chemie, XX, pp. 233-234, by Heidenreich, on this same problem. He proposes to avoid

the occluded ferric sulphate, by converting the iron by a suitable reducing medium, into the form of ferrous sulphate. He dissolves the pyrite in nitric acid, evaporates down three times with dilute hydrochloric acid, then adds hydrochloric acid, and filters into a 500 cc. Erlenmeyer flask, and dilutes the whole with hot water up to about 250 cc.. The required amount of metallic zinc is then added and a funnel placed in the mouth of the flask which is then heated gently on the sandbath. After the solution has become colorless, the iron reduced, and the zinc dissolved, the solution is filtered through a rapid filter into a glass beakerof one liter capacity and is washed well. The whole is taken up to about 600 cc. with hot water and heated, and precipitated with the requisite amount of barium chloride. The precipitate is allowed to stand twelve hours, after which it is filtered and washed with hot water every four or five minutes by decanting and then handled in the usual way. Heidenreich obtained almost uniform results, although some investigators have had trouble with the method.

By this method a new idea presents itself. Instead of using zinc, use iron reduced by hydrogen as a reducing agent. In this method the zinc sulphate is eliminated which seems to have given trouble. By employing iron as the reducing agent, the ferrous sulphate does no harm. Upon applying this modification of Heidenreich's method, very good results were obtained in every instance, and a method can undoubtedly be established involving this idea.

The conclusion of the results of the foregoing investigators on the question of determining sulphuric acid in the presence of iron, may be summed up in the following. When one precipitates sulphuric acid with barium chloride in hot solutions which contain ferric iron, the complex ion $Ba(Fe(SO_4)_2)_2$ is obtained. By this method a loss of as much as seven per cent may occur. The formation of this salt and the mistake in the analysis can be avoided by removing the ferric ions, and by keeping the conditions such that the complex salts do not form. The removing of the ferric ions can be accomplished by precipitating with ammonia, the filtering off of the precipitate being unnecessary, and by transforming into complex ions with ammonium

oxalates. By keeping the conditions such that the complex ferric sulphuric acid is formed, the barium sulphate is precipitated pure in two ways; first by precipitating cold, and secondly by precipitating the hot barium chloride with a mixture of ferric salt and sulphuric acid. Transforming the ferric iron into the ferrous state by reducing with zinc, does not lead to the desired end, because although ferric sulphuric acid salts do not form, and therefore the principal mistake is avoided, nevertheless small mistakes occur, namely in the mixture of zinc sulphate with barium sulphate. By using iron reduced by hydrogen, this error can be avoided. Four ways have been found of precipitating sulphuric acid as pure barium sulphate out of a solution in which iron is present in the highest de gree of oxidation. All of these were suggested by the application of the ion theory to the problem.